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EUTECTICS OF TRIAMINOGUANIDINE PERCHLORATE WITH LITHIUM PERCHLORATE AND PROPULSIVE METHOD

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This invention relates to derivatives of guanidine perchlorate, and more particularly, provides novel products comprising nitrogenous derivatives of guanidine perchlorate and methods of making the same.

Liquid propellants generally offer certain difficulties in storage and handling. For example, oxidants like liquid oxygen are volatile and corrosive materials, with handling characteristics such that they cannot be loaded into a rocket until just before it is to be fired. Difficulties with solid rocket propellant technology include the fact that the high solids loading of the propellant composition usually makes the propellant mix extremely viscous and therefore difficult to cast into a void-free propellant grain. Moreover, while the burning characteristics of the grain are usually improved by reducing the particle size of the solids phase of the material, comprising oxidants and other high energy materials, milling high energy materials to reduce the particle size is hazardous, and desirably avoided, particularly with impact sensitive materials.

Propellant compositions are made up of one or more fuels, and one or more oxidants. The perchlorates are a common oxidant in solid propellant manufacture. Among the metal perchlorates, lithium perchlorate is a preferred type, because of the low molecular weight of the metal salt byproduct of its decomposition, lithium chloride. It supplies 2 moles of oxygen per mole of the perchlorate in its decomposition, and the metal constitutes only about 5% of the weight of the perchlorate. Also, it is resistant to detonation by impact. However, since it supplies a non-gaseous salt as a byproduct, it is theoretically less advantageous as an oxidant than a perchlorate with an entirely non-metallic cation, decomposing to entirely gaseous products in combustion.

Triaminoguanidine perchlorate is a perchlorate with a nitrogenous cation which decomposes entirely into gaseous products in combustion. A factor operating against its adoption in propellant manufacture, however, is its great detonation sensitivity, which is below 5 centimeters (cm.), Bureau of Mines test (2 kilogram weight, 50% probability). Grinding or milling this material to reduce its particle size is too dangerous for it to be useful.

It is an object of this invention to provide novel perchlorate materials and methods of making the same.

A particular object of this invention is to provide novel perchlorate materials which can be employed in propellant manufacture with relative safety.

Still another object of this invention is to provide novel perchlorate salt materials which are liquid at relatively low temperatures, including room temperature.

A further object is to provide novel perchlorate materials, the combustion products of which are largely gaseous.

Still another object is to provide novel propellant materials.

These and other objects will become evident upon a consideration of the following specification and claims.

It has now been found that lithium perchlorate and triaminoguanidine perchlorate can advantageously be combined to form eutectics having unusual and useful properties.

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The lithium perchlorate/triaminoguanidine perchlorate eutectics are liquid at moderate temperatures, below about 100° C. The eutectic appearing at 35 weight percent triaminoguanidine perchlorate melts at 82° C. The eutectic at 65 weight percent triaminoguanidine perchlorate, it has now been found, has the unusual property, for a perchlorate salt material, of being a liquid at room temperature.

These eutectic materials have several significant advantages over their constituent materials. Considerably more of their combustion products are gaseous than is the case with lithium perchlorate, thus raising the specific impulse of the propellant materials. As compared to triaminoguanidine perchlorate, they are significantly less sensitive to impact, and in any case, since they can be handled as liquids at processing temperatures, the hazard of milling a solid to reduce particle size is obviated.

The fluidity of these perchlorate materials at moderate processing temperatures advantageously adapts them for use in a variety of propellant applications. Thus for example, these eutectics, particularly the 65 weight-percent triaminoguanidine perchlorate eutectic, may be used to supply a non-corrosive, non-volatile liquid propellant. This includes use as the oxidant for combustion of a reductant fuel, or indeed, as a liquid monopropellant, whereby the nitrogenous cation is oxidized by oxygen supplied by the anion to provide propulsive gases.

These novel materials also offer advantages in the manufacture of solid propellants. Where oxidant materials normally constitute a solid phase in a solid propellant mix, increasing its viscosity, the present perchlorate salt materials at moderate to low operating temperatures, instead increase the liquids phase of a propellant mix, so as to add to its fluidity. Thus the processing characteristics of a propellant mix are enhanced.

The solid propellant compositions in which the presently provided materials may be employed to advantage include solid solution propellants.

Solid solution propellants are polymeric solid solutions of an oxidizer, in which the oxidizer and polymer are in the same homogeneous phase. It has been found that such solid solutions can be prepared by polymerizing a monomer in the presence of dissolved lithium perchlorate, with the resulting polymeric product including in solution therein at least as much of the perchlorate as is in solution in the monomer mix. The polymeric solid solutions have several advantages. In the usual composite propellant, the plastic binder is a polymeric material serving as fuel, and oxidant to burn such fuel is combined with it as a separate phase of the heterogeneous product. The burning rate and stability to detonation are improved as the particle size of the oxidant is reduced, but milling the oxidant to reduce its particle size is hazardous. When the oxidant is in solid solution in the binder, intimate contact of fuel and binder is achieved without milling, and the solid solution has unexpectedly great resistance to detonation by impact.

Putting the oxidant into the same phase as the binder also raises the available solids loading of the composition. There is a limit to the solids loading for a given amount of binder, above which not enough binder will be available to form a continuous phase binding the discontinuous solids phase into a unitary structure. In the conventional composite propellant the solids phase includes oxidant for the binder. To the extent that the binder phase includes oxidant for itself, available solids loading is freed for the inclusion of other more energetic components. Thus propellants in which a polymeric solid solution of an oxidant is the binder have unusually low proportions of binder to total weight.

By polymerizing a polymerizable monomer in the presence of an oxidant amount of dissolved triaminoguanidine

dine perchlorate/lithium perchlorate eutectics as provided by this invention, impact-stable polymeric solid solutions of perchlorate oxidizer are provided which can advantageously be employed in the production of rocket propellants.

Referring now in more detail to a description of the stated eutectics of this invention, these novel products are perchlorate salt materials consisting essentially of triaminoguanidine perchlorate and lithium perchlorate, in a weight ratio selected from about 65:35 and about 35:65.

These novel materials will be made by combining the respective perchlorates in appropriate amounts. To provide true eutectics, wherein the perchlorates are more intimately associated than in a physical mixture, the perchlorates should be combined in the fluid state, in a melt or solution.

A simple and direct method preferred for making the present products consist simply of fusing the perchlorates together in the selected ratio. Making the liquid eutectic, containing 65 weight percent triaminoguanidine perchlorate, requires only that the perchlorates be mixed in the correct ratio: at room temperature, the two solids coalesce and liquefy upon stirring to provide the fluid product.

To use these eutectics as a rocket propellant, in a monopropellant system, they merely need to be ignited and fired. In a bipropellant system, the eutectics are combined with a fuel material, and supply the oxidant for combustion of the fuel in the firing. If this is a liquid system, the eutectic may be first contacted with the fuel in the firing chamber. In a solid system, the binder-fuel will be combined with the oxidant in the propellant grain, which is ignited when the system is to be fired.

The solid propellants of this invention will comprise polymeric binder and a eutectic as provided by this invention.

To prepare conventional composite solid propellants from these eutectics, the eutectic can be combined with a polymer binder and with other usual propellant ingredients such as burning rate controlling additives, by usual techniques such as milling and the like. In such case, polymers useful as binders may include hydrocarbons such as polyethylene or a polybutadiene rubber, halogenated polymers like vinyl chloride, vinylidene fluoride and so forth.

Propellant compositions can also be prepared in accordance with this invention by polymerizing a monomer in the presence of an oxidant amount of a dissolved eutectic of triaminoguanidine and lithium perchlorate as provided by this invention, thereby providing polymeric solid solutions of an oxidant amount of the eutectic with polymer in the same homogeneous phase.

By solid solution is meant that the perchlorate and the polymer are homogeneously mixed and in the same phase to the extent that heterogeneity therebetween is not evident on examination under an ocular microscope.

By a polymeric binder is meant a matrix comprising polymer having a molecular weight at least sufficient to make the polymer solid at room temperature. It is undesirable to have the molecular weight so high that the polymer is infusible and insoluble. Preferably the product will be sufficiently elastomeric to have a tensile strength of at least 50 pounds per square inch (p.s.i.).

For preparation of solid solution propellants, the perchlorate eutectic must be anhydrous, containing less than about 0.5 mole-percent water, and in reference to it, it is to be understood that anhydrous material is meant.

By an oxidant amount of the perchlorate eutectic is meant enough to supply the combustion oxidation requirements of a significant portion, which will be at least about half the oxidation requirements, of the polymer.

The oxidation requirements of the polymer may be supplied largely by the lithium perchlorate content of the triamino-guanidine perchlorate/lithium perchlorate

eutectic. Lithium perchlorate, LiClO_4 , decomposes to LiCl and 2 moles of oxygen molecules per mole of perchlorate. Thus referring for example to oxidation of the polymers including CH_2 and like hydrocarbon units, if the C atom forms CO and H atoms form water respectively, as gaseous oxidation products, the consumption of oxidant is 0.5 mole of lithium perchlorate per mole of methylene units so oxidized. Under certain conditions the hydrogen is not oxidized or is oxidized in part, but then a corresponding amount of metal is oxidized. Thus the ratio of lithium perchlorate to polymer to supply the oxidation requirements will be at least about 0.5 mole per mole of reduced carbon atoms in the polymer. The triaminoguanidine perchlorate content will supplement the lithium perchlorate in supplying oxygen for the oxidation requirements of the polymer to an extent depending on the amount of oxygen consumed in its own decomposition mechanism. In any case, to attain the benefits of this invention at least about half of the oxidation requirement of the polymer is to be supplied by dissolved eutectic in the same homogeneous phase as the polymer. Preferably all the oxygen requirement for the oxidation of the polymer is supplied by the dissolved perchlorate material, and still more preferably, more than half and desirably all the oxygen requirement of the total propellant composition is supplied by such perchlorate.

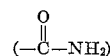
The polymeric solid solution compositions may consist essentially or entirely of the polymer and the triaminoguanidine perchlorate/lithium perchlorate eutectic. As will appear hereinafter, however, it is desirable to include other components in the composition. These may either be part of the same binder phase as the polymer, or part of the discontinuous solids phase combined with the binder. They may include fuels and oxidants, as further pointed out hereinafter. If these other compounds are fuels, they consume oxygen, and thus increase the total oxygen requirement of the composition. Where additional oxidant is included, the dissolved eutectic need not supply all the oxidant requirements of a composition, but to adapt the composition to propellant and fuel use, it is necessary that the composition include sufficient total oxidant to render combustion of the system self-supporting.

The quantity of perchlorate material desired in the final solid propellant composition will thus vary depending on the particular selection of ingredients. It may be up to about 80%, based on the total weight of the composition. It will be understood that substantially smaller amounts of the perchlorate material may be employed in effective compositions, and the amounts are often in the region of about 4 or 5 to 15 or 16 percent.

The polymerizable monomer system employed must polymerize without evolution of water, and dissolve or be miscible with at least an oxidant amount of presently provided novel perchlorate eutectic.

The polymerizable monomer systems available which polymerize without evolution of water include (1) vinyl monomers, susceptible to addition polymerization, such as acrylamide; (2) polyfunctional monomer mixtures, in which the monomers react to form polymers, such as mixtures of a diisocyanate with a glycol or diamine; and (3) homopolymerizing monomers, polymerizing by mechanisms which may be described as self-condensation, such as caprolactam.

To possess solvent power for the perchlorate oxidizer, it is found that the monomer should be a compound having a functional group including a donor atom selected from the group consisting of O, S and N. Combinations of such groups such as an amide group



in the monomer or polymer, are especially favorable.

Thus in addition polymerization, the polymerizable monomer will be an olefin containing a hetero donor atom selected from O, S and N. A preferred olefin type is an olefinic carbonamide, such as

acrylamide,
methacrylamide,
N-methylacrylamide,
N-tert-butylacrylamide,
N-tert-octylacrylamide,
N,N-dimethylacrylamide,
N,N-dipropylacrylamide,
N-octylmethacrylamide,
N-decylmethacrylamide,
1-vinyl-2-pyrrolidinone,
3-methyl-1-vinyl-2-pyrrolidinone,
3-butenic amide,

and the like. References herein to "an" acrylamide are intended to include both those in which the only non-hydrocarbon component is the carbonamide side chain group, such as those just mentioned, and those including additional hetero atoms selected from N, O and S, such as N-methylolacrylamide, N-(2-hydroxyethyl)acrylamide, 2-methylolacrylamide, N-acrylylmorpholine, N-methacrylylmorpholine, and N-(2-ethoxyethyl)acrylamide, N-(mercaptomethyl)acrylamide, 2-(2-ethylthioethyl)acrylamide and N-(tetrahydrothienyl)acrylamide, acrylic hydrazide, N-acrylylpiperazine, 2-(aminomethyl)acrylamide, 1-cyanoacrylamide, N-(trinitroethyl)acrylamide and the like.

The polymers in products of this invention can also be obtained from olefinic monomers susceptible to addition polymerization which are free of carbonamide bonds, such as 1-methoxybutadiene, vinylxyethanol, methyl vinyl ketone, methyl acrylate, tert-butyl acrylate, hexyl acrylate, and decyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, allyl acetate, vinyl formate, vinyl acetate and vinyl stearate, vinyl methyl sulfide, 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, ethylene glycol dimethacrylate, butylaminoethyl methacrylate, N,N-dimethylaminoethyl methacrylate and the like. Mixtures such as acrylamide-2-methoxyethyl acrylate, acrylamide-vinylxyethanol, acrylamide-acrylonitrile, acrylamide-allyl acetate, acrylamidevinyl formate, and so forth, may also be used.

As mentioned above, interreaction of two polyfunctional monomers is another useful kind of polymerization system. One monomer will have functional groups including active hydrogen, which may be a dihydric alcohol like ethylene glycol or propylene glycol, an amino alcohol like 2-aminoethanol or 3-aminopropanol, or a diamine like trimethylenediamine, N,N'-dimethylhexamethylenediamine, cyclohexanediamine, 2,2'-diaminoethanyl ether and sulfide, and so forth. The other polyfunctional monomer may be a diisocyanate such as hexamethylenediisocyanate or tolylenediisocyanate and the like, or a bisazlactone such as phenylenebis(4,4-dimethyl-2-oxazolin-5-one), or diepoxide such as 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate, the bis(epoxypropyl) ether of 2,2-bis(4-hydroxyphenyl)propane, the bis(epoxyexo-dihydrodicyclopentadienyl) ether of ethylene glycol, and so forth. The stated functional groups will be attached to polyvalent radicals which may be hydrocarbon, saturated aliphatic or aromatic unsaturated, or may include noninterfering hetero atoms such as O, N and S. The ratio of the monomers will be about such as to provide one active hydrogen functional group per functional group reactive to polymerize such group in the second monomer.

The self-condensing monomers polymerizing without evolution of water are illustrated by ϵ -caprolactam, 2-pyrrolidinone and like cyclic lactams, by diisocyanates such as hexamethylene diisocyanate or 4,4'-diisocyanatodiphenylmethane, optionally mixed with up to equimolar amounts of a monoisocyanate such as chlorophenyl iso-

cyanate, in systems forming polyisocyanurates, and so forth.

Polymerization conditions for polymerizing a monomer in the presence of a dissolved perchlorate eutectic in accordance with this invention are generally those usual for polymerizing the selected monomer, provided the system is anhydrous and includes solvent for dissolving the perchlorate eutectic. Temperatures should be below decomposition temperatures of the reaction mixture components, and usually not above 200° C. A temperature above 0° C., preferably above room temperature, and below 100° C., such as about 85° C. is preferred. Atmospheric pressures are preferred, but the pressure may be subatmospheric, down to 0.1 mm. Hg, or superatmospheric, up to 5000 p.s.i. Depending on the monomer system, polymerization may be spontaneous at temperatures of operation or in some cases may be catalyzed by the perchlorate material. If needed, usual polymerization catalysts for the system may be used, such as diazoisobutyronitrile as a free radical source in vinyl polymerization, ferric acetylacetonate and 1,4-diazobicyclo[2.2]octane in isocyanate polymerizations, and so forth. Polymerization conditions are maintained at least until solid polymer is formed.

Besides the polymer and perchlorate eutectic, additional components may be present in compositions embodying the present invention. For example, the polymerizable systems may and often desirably will include solvents and diluents which contribute useful plasticizing action to polymeric binders in which they are included, and also may promote solubility of the perchlorate material in the system. Useful plasticizers are illustrated by amides, including amides and hydrazides such as formamide, dimethylformamide, hydrazodicarbonamide and oxaldihydrazide, N-ethyl-p-toluenesulfonamide, N-ethyl-o-toluenesulfonamide, and so forth; glycols and ethers such as ethylene glycol, triethylene glycol dimethyl ether, ethylene glycol dimethyl ether and the like; plasticizers having good fuel properties and characterized by the presence of nitro groups, such as 5,5-dinitro-1,2-hexanediol, bis(2,2-dinitropropyl)-formal, 5,5 - dinitro - 1,3 - dioxane, tris-(hydroxymethyl)nitro methane, and so forth. The amount of plasticizer employed can vary up to about 35 weight percent of the polymer present in the composition but amounts of from about 15 to about 25 weight percent are generally preferred.

Also, the novel homogeneous, single-phase combinations of perchlorate eutectic with polymers provided by this invention can advantageously contain metal and hydride fuels. Thus for example, the propellant compositions may contain finely divided light metals and various hydrides thereof. Examples of these are beryllium, boron, magnesium, aluminum, magnesium hydride, aluminum hydride, the various solid hydrides such as decaborane and alkylated decaboranes (ethyl alkylated decaborane), aluminum borohydride, lithium aluminum hydride, and the like. For example, the homogeneous mixture of perchlorate eutectic and polymer may contain up to about 20% by weight of the total composition of atomized aluminum (particle size about 20 microns). Preferably the aforesaid fuel material should be sufficiently fine to all pass a standard 100 mesh screen, and more preferably should pass a 200 mesh screen.

These light metal and hydride high energy additives should preferably not exceed about 25 weight percent of the total composition, since the heavy combustion exhaust tends to lower performance of the solid propellant composition. It is often desirable to incorporate not more than from 5 to about 10 weight percent of said additives based on the total weight of the propellant composition.

Another group of additives which may be included in the system as part of the solids phase comprises oxidants, and other readily decomposable materials such as explosives. Illustrative of useful oxidants are, for example,

ammonium perchlorate, ammonium nitrate, additional (free, uncombined) lithium perchlorate and the like. Illustrative of useful explosives components are, for example, sodium azide.

The perchlorate-containing polymeric compositions of this invention burn vigorously and relatively uniformly when ignited and are useful as a solid propellant for rockets including short range ballistic weapons such as aircraft and artillery rockets and long range strategic missiles, wherein they may be the sole propellant or be employed in one or more stage of a multi-stage rocket system. When confined the aforesaid compositions also are particularly valuable as explosives.

The invention is illustrated but not limited by the following examples in which all parts are by weight unless otherwise noted.

Example 1

This example illustrates the preparation of the presently provided novel eutectics.

Triamino guanidine perchlorate is prepared by reacting guanidine perchlorate with hydrazine in a 1:3 molar ratio in isopropanol solution. The solvent must be evaporated off to isolate the triaminoguanidine perchlorate.

Mixes are now prepared of varying ratios of triaminoguanidine perchlorate and lithium perchlorate and the phase diagram of this system is prepared by heating the mixes to produce fusion, cooling to about room temperature, and then reheating to determine melting point. It is found that at a weight ratio of 35 parts triaminoguanidine perchlorate to 65 parts lithium perchlorate, a eutectic is formed which melts at 82° C. At the weight ratio of 65 parts triaminoguanidine perchlorate, 35 parts lithium perchlorate, the solids coalesce at room temperature, to form a clear, water white liquid.

Determination of the impact sensitivity of the triaminoguanidine perchlorate/lithium perchlorate eutectic melting at 82° C., by the Bureau of Mines test (50% probability, 2 kilogram weight) gives a value of 20 centimeters.

Example 2

This example illustrates the formation of a solid propellant employing a eutectic as provided by this invention.

A mix is prepared by combining 2 parts of N,N'-hexamethylenediamine with 2 parts of the liquid triaminoguanidine perchlorate/lithium perchlorate eutectic and 3.9 parts of 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy - 6 - methylcyclohexanecarboxylate. The mix is maintained at 90° C. for 30 minutes, when polymerization is complete. Cooling to room temperature provides a solid clear elastomeric product which will burn fiercely when ignited.

While the invention has been illustrated with reference to various specific embodiments thereof, it is to be appreciated that modification and variations are possible without departing from the scope of the invention, which is limited only as defined in the appended claims.

What is claimed is:

1. A eutectic consisting essentially of triaminoguanidine perchlorate and lithium perchlorate, in which the weight ratio of said perchlorates is selected from about 35:65 and about 65:35.

dine perchlorate and lithium perchlorate, in which the weight ratio of said perchlorates is selected from about 35:65 and about 65:35.

2. A liquid perchlorate salt eutectic consisting essentially of 65 weight percent triaminoguanidine perchlorate and 35 weight percent lithium perchlorate.

3. The method of propelling a rocket which comprises burning a propellant material comprising a eutectic as defined in claim 1 in the combustion chamber of a rocket.

4. A propellant composition comprising polymer and an oxidant amount of an intimate combination of triaminoguanidine perchlorate and lithium perchlorate as defined in claim 1.

5. The method of forming a polymeric solid solution of perchlorate wherein said perchlorate and polymer are in the same homogeneous phase which comprises polymerizing a polymerizable monomer including a donor atom selected from the group consisting of O, S, and N, in the presence of a dissolved eutectic of triaminoguanidine perchlorate and lithium perchlorate.

6. A propellant composition comprising a polymeric solid solution of perchlorate wherein said perchlorate and polymer are in the same homogeneous phase, said polymer being the polymer of a polymerizable monomer including a donor atom selected from the group consisting of O, S, and N, and said perchlorate being an intimate combination of triaminoguanidine perchlorate and lithium perchlorate as defined in claim 1, said propellant composition including an oxidant amount of said perchlorate.

7. A propellant composition comprising a polymeric solid solution of perchlorate wherein said perchlorate and polymer are in the same homogeneous phase, wherein said polymer is the product of reaction of a diamine with a diepoxide and said perchlorate is an intimate combination of triaminoguanidine perchlorate and lithium perchlorate as defined in claim 1, said perchlorate being present in an oxidant amount.

8. The method of forming a polymeric solid solution of perchlorate wherein said perchlorate and polymer are in the same homogeneous phase which comprises reacting a diamine with a diepoxide to form a polymer in the presence of a dissolved eutectic of triaminoguanidine perchlorate and lithium perchlorate.

9. The method of forming a polymeric solid solution of perchlorate wherein said perchlorate and polymer are in the same homogeneous phase which comprises heating a mixture of a diamine, a diepoxide and the liquid 65:35 weight ratio triaminoguanidine perchlorate/lithium perchlorate eutectic until formation of a polymer by reaction of said diamine with said diepoxide has occurred.

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